CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-3-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 2 hours **Maximum Marks: 35**

General Instructions

(i) This question paper contains **12** questions. **All** questions are compulsory.

(ii) This question paper is divided into **three** Sections – Section **A**, **B** and **C**.

(iii) **Section - A** Q. Nos. **1** to **3** are very short answer type questions carrying **2** marks each.

(iv) **Section - B** Q. Nos. **4** to **11** are short answer type questions carrying **3** marks each.

(v) **Section - C** Q. No. **12** is case based question carrying **5** marks.

(vi) Use of log tables and calculators is NOT allowed.

Section A (6 marks)

1. Predict the reagent for carrying out the following transformations: (Any two)

(i) Benzoyl chloride to Benzaldehyde

(ii) Ethanal to 3-hydroxy butanal

(iii) Ethanoic acid to 2-chloroethanoic acid [2 marks]

Solution:

Concept:

- Rosenmund reduction converts an acid chloride into an aldehyde using hydrogen over a poisoned palladium catalyst.
- Aldol addition joins two aldehyde molecules having alpha-hydrogen atoms in dilute base; the initial product is a beta-hydroxy aldehyde.
- The Hell–Volhard–Zelinsky reaction replaces an alpha-hydrogen of a carboxylic acid by a halogen.

Step 1: Select the reagent for transformation (i) Benzoyl chloride must be reduced only as far as benzaldehyde. Use H_2 with palladium supported on barium sulphate, $Pd/BaSO_4$, suitably poisoned. This is Rosenmund reduction:

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

The poisoned catalyst limits further reduction of the aldehyde to the alcohol.

Step 2: Select the reagent for transformation (ii) Treat ethanal with cold, dilute aqueous NaOH. Its alpha-hydrogen permits aldol addition, giving 3-hydroxybutanal:

$$2\,CH_3CHO \xrightarrow[\text{cold}]{\text{dil}\cdot\ NaOH} CH_3CH(OH)CH_2CHO.$$

Avoid heating the aldol product, since dehydration would give an unsaturated aldehyde instead of the required hydroxy aldehyde.

Step 3: Select the reagent for transformation (iii) Use Cl_2 in the presence of red phosphorus, followed by hydrolysis. Alpha-chlorination by the Hell–Volhard–Zelinsky reaction gives:

$$CH_3COOH + Cl_2 \xrightarrow{\text{red P}} ClCH_2COOH + HCl.$$

Chlorine replaces an alpha-hydrogen while the carboxyl group is retained.

Step 4: Conclusion The reagents are (i) H_2/poisoned $Pd/BaSO_4$; (ii) cold, dilute NaOH; and (iii) Cl_2/red phosphorus followed by hydrolysis. Any two transformations may be answered.

Quick Tip to Solve: Match the change first: acid chloride to aldehyde means Rosenmund reduction; a beta-hydroxy aldehyde means cold aldol conditions; alpha-chlorination of an acid means Cl_2/red phosphorus.

2. (i) Why on dilution the Λ_m of CH_3COOH increases very fast, while that of CH_3COONa increases gradually?

(ii) What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

[2 marks]

Solution:

Concept:

- Molar conductivity, Λ_m, measures the conductance due to the ions supplied by one mole of electrolyte. Its change on dilution depends on both ionisation and ionic mobility.
- A weak electrolyte ionises further on dilution, whereas a strong electrolyte is already almost completely dissociated.
- An external potential opposing a galvanic cell reverses the cell reaction when it exceeds the cell emf.

Step 1: Explain the different rates of increase in part (i) Ethanoic acid, CH_3COOH, is a weak electrolyte. On dilution, its degree of ionisation rises considerably, as shown by the equilibrium:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+.$$

The number of ions furnished per mole therefore increases markedly, so Λ_m increases rapidly. In contrast, sodium ethanoate, CH_3COONa, is a strong electrolyte and is already almost fully dissociated into CH_3COO^- and Na^+. Dilution mainly reduces interionic attractions and increases ionic mobility, so its Λ_m increases only gradually.

Step 2: Determine the effect of the external potential in part (ii) Consider the applied external potential opposing the cell emf. When this potential becomes greater than E°_{cell} under standard conditions, it drives electrons opposite to their spontaneous direction. The spontaneous galvanic reaction is reversed: the species previously undergoing reduction is oxidised, and the species previously oxidised is reduced. Electrical energy is consumed to drive this non-spontaneous reaction, so the cell operates as an electrolytic cell.

Step 3: Conclusion (i) CH_3COOH shows a rapid increase in Λ_m because dilution greatly increases ionisation; CH_3COONa shows a gradual increase mainly due to improved ionic mobility. (ii) A greater opposing external potential reverses the reaction and makes the cell electrolytic.

Quick Tip to Solve: Compare ions per mole when discussing molar conductivity: weak electrolytes gain many ions on dilution, while strong electrolytes mainly gain ionic mobility.

3. An Organic compound (A) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (B). Compound (B) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (C) and on reacting with $C_6H_5SO_2Cl$ forms a compound (D) which is soluble in alkali. Write the structures of (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into a primary amine, RNH_2, with one fewer carbon atom.
- A primary amine gives a foul-smelling isocyanide with $CHCl_3$ and alcoholic KOH; this is the carbylamine reaction.
- A primary amine reacts with benzenesulphonyl chloride to give a sulphonamide containing an acidic N–H bond, making the product soluble in alkali.

Step 1: Identify the amide and its degradation product Reaction with Br_2 and KOH indicates Hofmann degradation of a primary amide. The amide matching C_3H_7NO is propanamide, $CH_3CH_2C(=O)NH_2$. Removal of its carbonyl carbon produces ethanamine:

$$\begin{aligned} &CH_3CH_2CONH_2 + Br_2 + 4\,KOH \\ &\longrightarrow CH_3CH_2NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O. \end{aligned}$$

This establishes the two-carbon primary amine required for the subsequent tests.

Step 2: Apply the carbylamine reaction Ethanamine reacts with chloroform and alcoholic alkali on heating to give ethyl isocyanide. The ethyl group bonds to nitrogen, unlike a nitrile in which it bonds to carbon:

$$\begin{aligned} &CH_3CH_2NH_2 + CHCl_3 + 3\,KOH \\ &\longrightarrow CH_3CH_2NC + 3\,KCl + 3\,H_2O. \end{aligned}$$

The isocyanide group can be written as $-N^+\equiv C^-$, showing its nitrogen attachment explicitly.

Step 3: Apply the Hinsberg reaction Reaction with benzenesulphonyl chloride forms N-ethylbenzenesulphonamide:

$$CH_3CH_2NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHCH_2CH_3 + HCl.$$

The product retains an N–H hydrogen. Its removal by alkali forms an ionic salt, accounting for the stated solubility and confirming that the starting amine is primary.

Step 4: Conclusion The required condensed structures are:

(A)	$CH_3CH_2C(=O)NH_2$	propanamide,
(B)	$CH_3CH_2NH_2$	ethanamine,
(C)	$CH_3CH_2-N^+\equiv C^-$	ethyl isocyanide,
(D)	$C_6H_5SO_2NHCH_2CH_3$	N-ethylbenzenesulphonamide.

Quick Tip to Solve: In Hofmann degradation, subtract the carbonyl carbon before writing the amine. In the carbylamine product, attach the alkyl group to nitrogen: R–NC, not R–CN.

Section B (24 marks)

4. Account for the following:

(i) Cu^{2+} salts are coloured while Zn^{2+} salts are white.

(ii) E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(iii) Transition metals form alloys. [3 marks]

Solution:

Concept:

- Colour in many transition-metal ions arises from absorption of visible light during electronic transitions between split d orbitals. A partially filled d subshell permits such transitions.
- A standard reduction potential measures the tendency of a species to accept electrons. The relative stability of the oxidised and reduced electronic configurations helps explain its value.
- Metals with similar atomic sizes can replace one another in a metallic crystal, forming a solid solution called an alloy.

Step 1: (i) Compare the electronic configurations The configurations are $Cu^{2+} : [Ar]\,3d^9$ and $Zn^{2+} : [Ar]\,3d^{10}$. In the surrounding ligand field, the d orbitals of Cu^{2+} split into groups of different energies. Absorption of visible light promotes an electron between these levels; the remaining transmitted or reflected light gives the salt its colour. The d subshell of Zn^{2+} is completely filled, so these d-d transitions are unavailable. Its salts with colourless anions are consequently white as solids and colourless in solution.

Step 2: (ii) Compare the stability before and after reduction For manganese, the reduction is

$$Mn^{3+} + e^- \longrightarrow Mn^{2+}, \qquad 3d^4 \longrightarrow 3d^5.$$

It produces the particularly stable half-filled $3d^5$ configuration, so Mn^{3+} readily accepts an electron. For chromium, the corresponding reduction is

$$Cr^{3+} + e^- \longrightarrow Cr^{2+}, \qquad 3d^3 \longrightarrow 3d^4.$$

The Cr^{3+} ion has a stable $3d^3$ configuration, with favourable t_{2g}^3 occupancy in its octahedral aqueous complex. Reduction loses this stability. Thus reduction is much more favourable for the manganese couple, giving it the more positive E°.

Step 3: (iii) Relate alloy formation to atomic size Transition metals have similar atomic radii and often similar crystal structures. An atom of one transition metal can therefore occupy the lattice position of another without greatly disturbing the metallic structure. Their compatible metallic bonding allows these mixed crystals to remain stable, so transition metals readily form alloys with one another.

Step 4: Conclusion The colour contrast follows from $3d^9$ versus $3d^{10}$ occupancy; the potential contrast follows from the stability of Mn^{2+} and Cr^{3+}; and alloy formation follows chiefly from similar atomic sizes and compatible metallic lattices.

Quick Tip to Solve: For colour and reduction-potential questions, first write the ion's d-electron count; for alloys, compare atomic sizes rather than oxidation states.

5(a). Calculate $\Delta_r G^\circ$ and log K_c for the following cell:

$Ni(s) + 2\ Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

Given that $E^\circ_{cell} = 1.05$ V, 1F = 96,500 C mol^{-1}. [3 marks]

Solution:

Concept:

- The standard Gibbs energy change of a cell reaction is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per reaction as written and F is the Faraday constant.
- At equilibrium, $\Delta_r G^\circ = -RT\ln K_c = -2.303RT\log K_c$. Here R is the gas constant, T is absolute temperature and $\log$ denotes the base-ten logarithm.
- At the usual tabulation temperature of $298\,\text{K}$, the two relations give $E^\circ_{\text{cell}} = (0.0591/n)\log K_c$, with the potential in volts.

Step 1: Count the electrons transferred Separate the given reaction into oxidation at the nickel electrode and reduction at the silver electrode:

$$\begin{aligned} \text{Ni}\,(\text{s}) &\longrightarrow \text{Ni}^{2+}(\text{aq}) + 2\,\text{e}^-, \\ 2\,\text{Ag}^+(\text{aq}) + 2\,\text{e}^- &\longrightarrow 2\,\text{Ag}\,(\text{s}). \end{aligned}$$

Two electrons are transferred per mole of the reaction as written, so $n = 2$. Adding the half-reactions cancels these electrons and reproduces the stated cell reaction.

Step 2: Substitute in the Gibbs energy relation Use the supplied potential and Faraday constant without multiplying the potential by a stoichiometric coefficient:

$$\begin{aligned} \Delta_r G^\circ &= -2 \times 96500 \times 1.05\,\text{J mol}^{-1} \\ &= -202650\,\text{J mol}^{-1} \\ &= -202.65\,\text{kJ mol}^{-1}. \end{aligned}$$

The units follow from $1\,\text{C} \times 1\,\text{V} = 1\,\text{J}$. The negative sign is consistent with the positive standard cell potential.

Step 3: Relate the potential to the equilibrium constant Equating the two expressions for standard Gibbs energy gives

$$\log K_c = \frac{nFE^\circ_{\text{cell}}}{2.303RT}.$$

Taking the standard cell potential at the conventional $298\,\text{K}$ tabulation temperature,

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 1.05}{0.0591} \approx 35.53.$$

The large positive logarithm means that the equilibrium strongly favours the products of the stated reaction. Pure solid nickel and silver have unit activities and do not enter the equilibrium expression.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -202.65\,\text{kJ mol}^{-1}}$ and, at $298\,\text{K}$, $\boxed{\log K_c \approx 35.5}$.

Quick Tip to Solve: Read $n = 2$ from nickel changing from oxidation state zero to $+2$; use that same n in both formulae and convert joules to kilojoules only at the end.

OR

5(b). Calculate the e.m.f. of the following cell at 298 K:

Fe(s) | Fe^{2+} (0.001 M) || H^+ (0.01 M) | H_2(g) (1 bar) | Pt(s)

Given that E°_{cell} = +0.44 V

[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1] [3 marks]

Solution:

Concept:

- For a cell at 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- In Q, pure solids have unit activity. Dissolved ions contribute their concentrations relative to the standard concentration, and a gas contributes its pressure relative to 1 bar.

Step 1: Write the cell reaction and identify electron transfer The left electrode is the anode, where iron is oxidised. At the right electrode, hydrogen ions are reduced on the inert platinum surface:

$$\begin{aligned} \text{Anode:} \quad & \mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-} \\ \text{Cathode:} \quad & 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)} \\ \text{Overall:} \quad & \mathrm{Fe(s)} + 2\,\mathrm{H^+(aq)} \longrightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{H_2(g)}. \end{aligned}$$

Thus, $n = 2$. Platinum provides a conducting surface and does not appear in the net reaction.

Step 2: Evaluate the reaction quotient The coefficient 2 of the hydrogen ions becomes the exponent in the denominator. Iron metal is omitted because it is a pure solid. Using the given concentrations in mol L^{-1} and hydrogen pressure in bar gives

$$Q = \frac{[\mathrm{Fe^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

The concentrations in this expression are understood relative to 1 mol L^{-1}, so Q is dimensionless. Consequently, $\log Q = \log 10 = 1$.

Step 3: Substitute in the Nernst equation With $E^\circ_{\text{cell}} = +0.44\,\mathrm{V}$, the concentration correction is

$$E_{\text{cell}} = 0.44 - \frac{0.0591}{2}(1) = 0.44 - 0.02955 = 0.41045\,\mathrm{V}.$$

Since $Q > 1$, the correction lowers the cell potential below its standard value, consistent with the sign in the Nernst equation.

Step 4: Conclusion The e.m.f. of the cell at 298 K is $\boxed{E_{\text{cell}} \approx +0.410\,\mathrm{V}}$.

Quick Tip to Solve: First balance the hydrogen half-reaction: its two hydrogen ions mean both $n = 2$ and a squared hydrogen-ion concentration in Q.

6. (a) Using valence bond theory, predict the hybridization and magnetic character of following: $[CoF_6]^{3-}$ [Atomic number of Co = 27]

(b) Write IUPAC name of the following complex: $[CoBr_2(en)_2]^+$

(c) How many ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in solution? [3 marks]

Solution:

Concept:

- In valence bond theory, a six-coordinate complex is octahedral. Weak-field ligands may leave the metal's $3d$ electrons unpaired, giving outer-orbital sp^3d^2 hybridisation; unpaired electrons produce paramagnetism.
- For coordination nomenclature, name ligands alphabetically before the metal and indicate the metal's oxidation state in Roman numerals. A polydentate ligand with a complex name uses multiplicative prefixes such as bis.
- On dissolution, counter-ions outside the coordination brackets separate from the intact complex ion; coordinated ligands inside the brackets are not counted as free ions.

Step 1: Determine the electronic configuration for part (a) Let cobalt's oxidation state in $[CoF_6]^{3-}$ be x. Each fluorido ligand has charge -1, so $x - 6 = -3$, giving $x = +3$. Neutral cobalt has configuration $[Ar]\,3d^7 4s^2$; removing the two $4s$ electrons and one $3d$ electron gives Co^{3+} : $[Ar]\,3d^6$.

Step 2: Apply valence bond theory to part (a) The fluorido ligand is weak-field and does not cause additional pairing of the $3d$ electrons. The six $3d$ electrons therefore occupy the five orbitals with occupancies $2, 1, 1, 1, 1$, leaving four unpaired electrons. Two vacant inner $3d$ orbitals are consequently unavailable. One $4s$, three $4p$ and two $4d$ orbitals hybridise to form six sp^3d^2 orbitals which accept ligand lone pairs. The complex is thus an outer-orbital octahedral complex, and the four unpaired electrons make it paramagnetic.

Step 3: Construct the IUPAC name for part (b) In $[CoBr_2(en)_2]^+$, each bromido ligand has charge -1, while en (ethane-1,2-diamine) is neutral. Thus, $x - 2 = +1$, so cobalt is in oxidation state $+3$. Alphabetically, bromido precedes ethane-1,2-diamine; the two en ligands are expressed as bis(ethane-1,2-diamine). Because this is a complex cation, the metal retains the name cobalt. Combining these gives dibromidobis(ethane-1,2-diamine)cobalt(III) ion.

Step 4: Count the ions released in part (c) The two chloride ions lie outside the coordination sphere, whereas all six neutral ammine ligands remain coordinated. The dissociation is

$$[Co(NH_3)_6]Cl_2 \longrightarrow [Co(NH_3)_6]^{2+} + 2\,Cl^-.$$

One formula unit therefore yields one complex cation and two chloride anions, giving $1 + 2 = 3$ ions in solution.

Step 5: Conclusion (a) $\boxed{sp^3d^2}$ hybridisation; paramagnetic with four unpaired electrons. (b) Dibromidobis(ethane-1,2-diamine)cobalt(III) ion. (c) $\boxed{3\text{ ions}}$ per formula unit.

Quick Tip to Solve: For the ion count, keep everything inside the square brackets together: the printed two outside chlorides give one complex ion plus two counter-ions.

7(a). Differentiate between the following:

(i) Adsorption and Absorption

(ii) Lyophobic Sol and Lyophilic Sol

(iii) Multimolecular Colloid and Macromolecular colloid. [3 marks]

Solution:

Concept:

- Sorption processes are distinguished by where the substance accumulates: the surface or the bulk of another substance.
- Sols are classified as lyophilic or lyophobic according to the affinity between their dispersed phase and dispersion medium.
- A colloidal particle may be an aggregate of many small units or a single large molecule; this distinguishes multimolecular and macromolecular colloids.

Step 1: (i) Compare adsorption with absorption In adsorption, molecules of a substance accumulate on the surface of another substance. It is a surface phenomenon, so the concentration of the adsorbed substance is higher at the surface than in the bulk. For example, activated charcoal adsorbs gases on its surface.

In absorption, the substance penetrates and is distributed throughout the bulk of another substance. It is therefore a bulk phenomenon. For example, water is absorbed by a sponge.

Step 2: (ii) Compare lyophobic and lyophilic sols In a lyophobic sol, the dispersed particles have little affinity for the dispersion medium. Such sols require special preparation methods, are relatively unstable, and are readily coagulated by adding small amounts of an electrolyte. They are generally irreversible: adding the medium to the separated dispersed phase does not readily regenerate the sol. Gold sol in water is an example.

In a lyophilic sol, the dispersed phase has strong affinity for the medium. The particles are strongly solvated, making the sol comparatively stable. Such sols are generally reversible and need a much larger quantity of electrolyte for coagulation. Starch sol in water is an example.

Step 3: (iii) Compare multimolecular and macromolecular colloids A multimolecular colloid forms when many small atoms or molecules aggregate to form a particle of colloidal size. The individual units are held together mainly by van der Waals forces. Gold sol and sulphur sol are examples; a sulphur-sol particle contains many S_8 molecules.

In a macromolecular colloid, each particle is a single molecule of very high molecular mass whose size already lies in the colloidal range. Such molecules form colloidal solutions in suitable solvents. Starch, proteins and cellulose are examples of macromolecules.

Step 4: Conclusion The essential distinctions are surface accumulation versus bulk penetration, little versus strong affinity for the medium, and an aggregate of small units versus a single large molecule, respectively.

Quick Tip to Solve: Compare each pair on one common basis: location for sorption, affinity for sols, and the number of molecules making one colloidal particle.

OR

7(b). (I) Define the following terms:

(i) Zeta Potential

(ii) Coagulation

(II) Why a negatively charged sol is obtained when $AgNO_3$ solution is added to KI solution? [3 marks]

Solution:

Concept:

- A charged colloidal particle attracts oppositely charged ions from the dispersion medium, producing an electrical double layer.
- Repulsion between similarly charged particles helps stabilise a sol. Removing this repulsion allows the particles to aggregate and settle.
- A freshly formed precipitate preferentially adsorbs an ion common to its composition when that ion is present in excess in the surrounding solution.

Step 1: (I)(i) Define zeta potential The electrical potential difference between the fixed layer of ions associated with a colloidal particle and the diffused layer of counter-ions is called the zeta potential, or electrokinetic potential. The fixed layer moves with the particle, while the more loosely held counter-ions form the diffused layer in the surrounding medium. The two layers together constitute the electrical double layer.

Step 2: (I)(ii) Define coagulation Coagulation is the process of precipitation of colloidal particles by their aggregation into larger particles that settle out. For example, adding a suitable electrolyte supplies counter-ions that reduce or neutralise the particles' charge. The resulting decrease in electrostatic repulsion allows the dispersed particles to come together and form a precipitate.

Step 3: (II) Identify the ion adsorbed by silver iodide On adding silver nitrate solution to potassium iodide solution, silver iodide is formed:

$$\mathrm{AgNO_3(aq) + KI(aq) \longrightarrow AgI(s) + KNO_3(aq).}$$

Since silver nitrate is added to potassium iodide, iodide ions are present in excess in the receiving solution. The freshly formed AgI particles preferentially adsorb these I^- ions, which are common to the precipitate, rather than K^+ ions. The adsorbed iodide ions impart a negative charge to the particles; potassium ions act as counter-ions in the surrounding medium. Thus the sign of the sol's charge is determined by the excess constituent ion that is adsorbed.

Step 4: Conclusion Zeta potential is the potential difference between the fixed and diffused ionic layers. Coagulation is the precipitation of colloidal particles through aggregation. The AgI sol is negatively charged because its particles preferentially adsorb excess I^- ions from the KI solution.

Quick Tip to Solve: For an AgI sol, identify the excess reactant: excess KI supplies adsorbed I^- and gives negative particles, while excess $AgNO_3$ supplies adsorbed Ag^+ and gives positive particles.

8. Define transition metals. Why Zn, Cd and Hg are not called transition metals? How is the variability in oxidation states of transition metals different from that of p-block elements? [3 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its ground-state atom or in at least one of its common oxidation states.
- The $(n-1)d$ and ns orbitals of transition metals have comparable energies, so different numbers of their electrons can participate in bonding.

Step 1: State the definition of transition metals Transition metals are metallic elements whose atoms, or ions in a common oxidation state, contain an incompletely filled d subshell. Thus, merely belonging to the d-block is insufficient: the electronic configuration must satisfy this criterion.

Step 2: Examine zinc, cadmium and mercury The relevant ground-state configurations are

$$\begin{aligned} \mathrm{Zn} &: [\mathrm{Ar}]\, 3d^{10}4s^2, \\ \mathrm{Cd} &: [\mathrm{Kr}]\, 4d^{10}5s^2, \\ \mathrm{Hg} &: [\mathrm{Xe}]\, 4f^{14}5d^{10}6s^2. \end{aligned}$$

Their atoms have completely filled d subshells. On losing the two outer s electrons, their usual divalent ions also retain d^{10} configurations: Zn^{2+} is $3d^{10}$, Cd^{2+} is $4d^{10}$ and Hg^{2+} is $5d^{10}$. They therefore do not meet the transition-metal criterion in their common oxidation states.

Step 3: Compare the changes in oxidation state Transition metals commonly show several oxidation states differing by one unit, because both ns and $(n-1)d$ electrons can participate in bonding. For example, manganese exhibits $+2, +3, +4, +5, +6$ and $+7$. The common variable oxidation states of p-block elements usually differ by two units. This reflects participation or non-participation of the outer ns^2 electron pair in bonding; for example, tin shows $+2$ and $+4$, while lead shows $+2$ and $+4$. The greater stability of the lower state down a group is associated with the inert-pair effect.

Step 4: Conclusion Transition metals require a partially filled d subshell in the atom or a common ion. Zn, Cd and Hg retain filled d^{10} subshells and are excluded. Transition-metal oxidation states commonly differ by one unit, whereas the common variable states of p-block elements generally differ by two.

Quick Tip to Solve: Check the atom and its common ions for d^1 to d^9; a filled d^{10} subshell alone does not establish transition-metal character.

9(a). What happens when

(i) Propanone is treated with CH_3MgBr and then hydrolysed?

(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction? [3 marks]

Solution:

Concept:

- Grignard reagents add an alkyl group to the carbonyl carbon; hydrolysis of the resulting magnesium alkoxide gives an alcohol.
- An aldehyde reacts with excess alcohol in the presence of an acid catalyst to form an acetal, with elimination of water.
- Aldehydes lacking an α-hydrogen undergo the Cannizzaro reaction in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Add methylmagnesium bromide to propanone (i) In dry ether, the methyl group from CH_3MgBr attacks the carbonyl carbon of propanone, producing a magnesium alkoxide:

$$CH_3COCH_3 + CH_3MgBr \xrightarrow{\text{dry ether}} (CH_3)_3C{-}OMgBr.$$

Hydrolysis replaces the magnesium-containing group on oxygen by hydrogen:

$$(CH_3)_3C{-}OMgBr + H_2O \longrightarrow (CH_3)_3COH + Mg(OH)Br.$$

The product is 2-methylpropan-2-ol (tert-butyl alcohol), a tertiary alcohol: the carbon bearing the hydroxyl group has three methyl groups.

Step 2: Form the acetal of ethanal (ii) Ethanal first adds one molecule of ethanol to give a hemiacetal. In the presence of acid and excess ethanol, reaction with a second ethanol molecule forms the acetal:

$$CH_3CHO + 2\,C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3CH(OC_2H_5)_2 + H_2O.$$

The product is 1,1-diethoxyethane (ethanal diethyl acetal). Its two ethoxy groups are on the original carbonyl carbon. Excess ethanol favours acetal formation.

Step 3: Disproportionate methanal in concentrated alkali (iii) Methanal has no α-carbon and hence no α-hydrogen. On treatment with concentrated sodium hydroxide, two methanal molecules undergo disproportionation:

$$2\,HCHO + NaOH \xrightarrow{\text{conc.}} HCOONa + CH_3OH.$$

One molecule is oxidised to sodium methanoate (sodium formate), while the other is reduced to methanol. The alkaline medium gives the carboxylate salt, rather than the free acid.

Step 4: Conclusion (i) Propanone gives 2-methylpropan-2-ol, $(CH_3)_3COH$. (ii) Ethanal gives 1,1-diethoxyethane, $CH_3CH(OC_2H_5)_2$. (iii) Methanal gives methanol and sodium methanoate with concentrated $NaOH$.

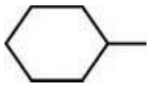
Quick Tip to Solve: Count the added methyl group for the Grignard product, put two ethoxy groups on the aldehyde carbon for the acetal, and pair an alcohol with a carboxylate salt for Cannizzaro.

OR

9(b). Write the main product in the following reactions:

(i) $2\,CH_3COCl + (CH_3)_2Cd \longrightarrow$

(ii) $CH_3CH_2CHO \xrightarrow{\text{Zn(Hg)/Conc. HCl}}$ [3 marks]

(iii)  $\text{COONa} + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}}$

Solution:

Concept:

- Dialkylcadmium reacts with an acyl chloride to form a ketone: the chlorine of the acyl chloride is replaced by an alkyl group.
- Clemmensen reduction, using zinc amalgam and concentrated HCl, converts the carbonyl group of an aldehyde or ketone into a methylene group.
- Heating a sodium carboxylate with soda lime, $NaOH$ and CaO, removes the carboxyl carbon as carbonate: $RCOONa + NaOH \longrightarrow RH + Na_2CO_3$.

Step 1: (i) Replace acyl chlorine by methyl Each methyl group of dimethylcadmium replaces the chlorine atom of one molecule of ethanoyl chloride. The carbonyl group remains intact, giving the ketone propanone:

$$2\,CH_3COCl + (CH_3)_2Cd \longrightarrow 2\,CH_3COCH_3 + CdCl_2.$$

The reagent reacts selectively to form the ketone; further addition to produce a tertiary alcohol does not occur under these conditions.

Step 2: (ii) Reduce the aldehyde group The terminal $-CHO$ group of propanal is reduced to $-CH_3$ by $Zn(Hg)$ and concentrated HCl. No carbon atom is removed from the chain:

$$CH_3CH_2CHO + 4\,[H] \longrightarrow CH_3CH_2CH_3 + H_2O.$$

Thus the three-carbon aldehyde becomes the corresponding three-carbon alkane, propane.

Step 3: (iii) Decarboxylate the sodium salt The printed ring has only single bonds, so the reactant is sodium cyclohexanecarboxylate, $C_6H_{11}COONa$. Soda lime replaces its $-COONa$ group by hydrogen while leaving the saturated six-membered ring intact:

$$C_6H_{11}COONa + NaOH \xrightarrow{CaO,\ \Delta} C_6H_{12} + Na_2CO_3.$$

The organic product is cyclohexane. Its six carbon atoms are those of the original ring; the seventh carbon, from the carboxylate group, enters sodium carbonate.

Step 4: Conclusion The main products are (i) propanone, CH_3COCH_3; (ii) propane, $CH_3CH_2CH_3$; and (iii) cyclohexane, C_6H_{12}.

Quick Tip to Solve: Match each reagent to its change: cadmium adds methyl, Clemmensen removes carbonyl oxygen, and soda lime removes the carboxyl carbon. Check whether the printed ring is saturated.

10. Give reasons:

(i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(ii) Aniline does not give Friedel-Crafts reaction.

(iii) Although –NH_2 group is o/p directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of m-nitroaniline. [3 marks]

Solution:

Concept:

- Amines contain a nitrogen lone pair and act as nucleophiles and Lewis bases. A primary amine formed by ammonolysis can undergo further alkylation.
- The free $-NH_2$ group activates an aromatic ring by resonance and directs electrophilic substitution to the ortho and para positions. Coordination or protonation of nitrogen changes this behaviour.

Step 1: (i) Follow successive alkylation during ammonolysis Ammonia attacks an alkyl halide to give a primary amine after deprotonation. However, the primary amine still has a nitrogen lone pair and reacts with further alkyl halide. Successive alkylation therefore produces secondary and tertiary amines and finally a quaternary ammonium salt:

$$NH_3 \longrightarrow RNH_2 \longrightarrow R_2NH \longrightarrow R_3N \longrightarrow R_4N^+X^-.$$

This schematic sequence represents successive reactions with RX, with deprotonation where required. The mixture of products is difficult to separate, so ammonolysis is unsuitable for obtaining a pure primary amine. Excess ammonia favours the primary amine but does not make the reaction completely selective.

Step 2: (ii) Account for the Lewis acid catalyst Friedel–Crafts reactions use a Lewis acid catalyst such as anhydrous $AlCl_3$. Aniline is a Lewis base: its nitrogen lone pair coordinates to $AlCl_3$, forming an aniline–aluminium chloride complex. The lone pair becomes unavailable for donation into the ring, and the complex strongly deactivates the ring towards electrophilic substitution. Consequently, aniline does not undergo the normal Friedel–Crafts reaction.

Step 3: (iii) Identify aniline's form in the nitrating mixture The strongly acidic nitrating mixture protonates aniline to form the anilinium ion:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3{}^+.$$

Unlike $-NH_2$, the $-NH_3{}^+$ group has no lone pair available for resonance donation and withdraws electron density from the ring. It is deactivating and meta directing; the ortho and para substitution intermediates are especially destabilised by the positively charged substituent. Nitration of the anilinium ion thus gives a substantial amount of meta-nitroaniline after work-up, even though unprotonated aniline is ortho/para directing.

Step 4: Conclusion (i) Repeated alkylation gives a mixture of amines and quaternary ammonium salt. (ii) Aniline forms a ring-deactivating complex with the Friedel–Crafts Lewis acid catalyst. (iii) In the acidic nitrating mixture, aniline forms the meta-directing anilinium ion, giving a good yield of meta-nitroaniline.

Quick Tip to Solve: Track the nitrogen lone pair: it causes further alkylation, binds the Friedel–Crafts catalyst, and accepts a proton during nitration. For nitration, determine the directing group after protonation.

11(a). (i) Which acid of the following pair would you expect to be stronger?

F-CH_2-COOH or CH_3-COOH

(ii) Arrange the following compounds in increasing order of their boiling points:

CH_3CH_2OH, CH_3-CHO, CH_3-COOH

(iii) Give simple chemical test to distinguish between Benzaldehyde and Acetophenone. [3 marks]

Solution:

Concept:

- An electron-withdrawing substituent stabilises a carboxylate ion by its negative inductive effect, thereby increasing the acidity of the parent acid.
- Boiling point rises with the strength of intermolecular attractions. Hydrogen bonding and association are especially important for alcohols and carboxylic acids.
- Tollens' reagent, ammoniacal silver nitrate, oxidises an aldehyde and is reduced to metallic silver; an ordinary ketone does not give this test.

Step 1: (i) Compare the stability of the conjugate bases Fluorine in FCH_2COOH withdraws electron density through sigma bonds because it is strongly electronegative. Its negative inductive effect stabilises the negative charge in the conjugate base FCH_2COO^-. In contrast, the methyl group of CH_3COOH has an electron-releasing inductive effect, which makes the acetate ion relatively less stable. Consequently, fluoroacetic acid loses a proton more readily than acetic acid.

Step 2: (ii) Identify the intermolecular attractions Ethanal has dipole–dipole attractions but cannot form hydrogen bonds between its own molecules because it has no hydrogen bonded to oxygen. Ethanol molecules form intermolecular hydrogen bonds. Ethanoic acid associates strongly through hydrogen-bonded dimers and requires more energy to separate its molecules. Thus, for these compounds, the increasing boiling-point order is

$$CH_3CHO < CH_3CH_2OH < CH_3COOH.$$

Step 3: (iii) Apply Tollens' test to separate samples Add freshly prepared Tollens' reagent to each sample and warm gently in a water bath. Benzaldehyde forms a silver mirror on the test-tube wall as it is oxidised to benzoate:

$$C_6H_5CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow C_6H_5COO^- + 2\,Ag + 4\,NH_3 + 2\,H_2O.$$

Acetophenone is a ketone and gives no silver mirror under these conditions. This difference in observation distinguishes the two compounds.

Step 4: Conclusion (i) FCH_2COOH is the stronger acid. (ii) The order is ethanal $<$ ethanol $<$ ethanoic acid. (iii) Benzaldehyde gives a silver mirror with Tollens' reagent, while acetophenone does not.

Quick Tip to Solve: For this pair use Tollens' test: benzaldehyde responds, whereas Fehling's test is unsuitable because aromatic aldehydes generally do not reduce it.

OR

11(b). (i) Which will undergo faster nucleophilic addition reaction? Acetaldehyde or Propanone
(ii) What is the composition of Fehling's reagent?
(iii) Draw structure of the semicarbazone of Ethanal. [3 marks]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electrophilic carbonyl carbon. Electron-releasing alkyl groups and steric crowding both decrease its reactivity towards a nucleophile.
- Fehling's reagent is a freshly prepared mixture of aqueous copper(II) sulphate and an alkaline solution of sodium potassium tartrate.
- Semicarbazide, $H_2N-NH-CO-NH_2$, condenses with a carbonyl compound through its terminal hydrazino $-NH_2$ group, eliminating water to form a semicarbazone.

Step 1: (i) Compare the carbonyl environments Acetaldehyde, CH_3CHO, has one methyl group and one hydrogen attached to the carbonyl carbon. Propanone, CH_3COCH_3, has two methyl groups. The two electron-releasing methyl groups in propanone reduce the partial positive charge on its carbonyl carbon more than the single methyl group in acetaldehyde. They also obstruct the approach of the nucleophile more strongly. Acetaldehyde therefore undergoes nucleophilic addition faster, owing to both electronic and steric factors.

Step 2: (ii) State the two components of Fehling's reagent Fehling's solution A is an aqueous solution of copper(II) sulphate, $CuSO_4$. Fehling's solution B is an alkaline solution of sodium potassium tartrate (Rochelle salt), prepared using sodium hydroxide. Equal volumes of A and B are mixed freshly before use. Tartrate complexes the copper(II) ions and keeps them in solution in the alkaline medium, producing the characteristic deep-blue reagent.

Step 3: (iii) Form and draw ethanal semicarbazone The terminal hydrazino amino group of semicarbazide reacts with the carbonyl group of ethanal. Condensation replaces the carbonyl C=O group by $C=N-NH-CO-NH_2$, with loss of one molecule of water:

$$CH_3CHO + H_2N-NH-CO-NH_2 \longrightarrow CH_3CH=N-NH-CO-NH_2 + H_2O.$$

The methyl group and the hydrogen originally attached to the aldehyde carbon remain attached to that carbon. The amide carbonyl in the semicarbazide portion remains unchanged, as shown in the structure below.

$$CH_3-CH=N-NH-\overset{\overset{O}{\|}}{C}-NH_2$$

Structure of ethanal semicarbazone

Step 4: Conclusion (i) Acetaldehyde reacts faster. (ii) Fehling's reagent contains aqueous copper(II) sulphate and alkaline sodium potassium tartrate. (iii) Ethanal semicarbazone is $CH_3CH=N-NH-CO-NH_2$.

Quick Tip to Solve: In a semicarbazone, retain the reagent's amide C=O group; only the aldehyde's carbonyl oxygen is replaced by $N-NH-CO-NH_2$.

Section C (5 marks)

12. Read the following passage and answer the questions that follow:

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law:

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reactions are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. [5 marks]

12(a). What is the effect of temperature on the rate constant of a reaction? [1 mark]

Solution:

Concept:

- The Arrhenius equation relates the rate constant to absolute temperature: $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy and R the gas constant.
- For an ordinary reaction with positive activation energy, increasing temperature increases the fraction of molecules with sufficient energy to react.

Step 1: Examine the temperature dependence As absolute temperature T increases, $E_a/(RT)$ decreases. The exponential factor $e^{-E_a/(RT)}$ therefore increases, so the rate constant increases for a fixed reaction.

Step 2: State the usual experimental trend For many reactions near ordinary temperatures, a rise of $10\,\text{K}$ approximately doubles the rate constant. This is a common empirical trend; the actual increase depends on the activation energy and temperature interval.

Step 3: Conclusion The rate constant generally increases with temperature, often becoming approximately twice as large for a $10\,\text{K}$ rise.

Quick Tip to Solve: In the Arrhenius expression, increasing T makes the negative exponent less negative, so k increases.

12(b). For a reaction $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{Product}$, the rate law is given by, $\mathrm{Rate} = k[\mathrm{A}]^2[\mathrm{B}]^{1/2}$. What is the order of the reaction? [1 mark]

Solution:

Concept:

- The overall order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- For $\mathrm{Rate} = k[\mathrm{A}]^x[\mathrm{B}]^y$, the individual orders are x and y; the overall order is $x + y$. Order may be fractional.

Step 1: Identify the concentration powers In the given law $\mathrm{Rate} = k[\mathrm{A}]^2[\mathrm{B}]^{1/2}$, the exponent of $[\mathrm{A}]$ is 2, and that of $[\mathrm{B}]$ is $1/2$. These give the individual orders with respect to A and B.

Step 2: Add the individual orders Use the exponents from the rate law, rather than the coefficients in the reaction equation:

$$n = 2 + \frac{1}{2} = \frac{5}{2}.$$

The rate constant k does not contribute another power to this sum.

Step 3: Conclusion The overall order of the reaction is $\boxed{\frac{5}{2} = 2.5}$.

Quick Tip to Solve: Read the powers of both concentrations in the rate law and add them; reaction coefficients do not determine order.

12(c). How order and molecularity are different for complex reactions? [1 mark]

Solution:

Concept:

- Order is the sum of concentration exponents in the experimental rate law and can be assigned to an overall complex reaction.
- Molecularity counts the reacting particles participating in a single elementary step; it is a positive whole number.

Step 1: Describe order for a complex reaction A complex reaction proceeds through several elementary steps. Its overall order is obtained from the experimentally observed rate law, which reflects its mechanism and rate-controlling step. Order can be zero, integral or fractional and cannot generally be read from the overall balanced equation.

Step 2: Restrict molecularity to elementary steps Each elementary step has its own molecularity, determined by how many reacting species participate in that step. The overall complex reaction has no defined molecularity because its net equation does not represent a single molecular event.

Step 3: Conclusion Order is defined experimentally for an overall complex reaction; molecularity is defined only for its individual elementary steps, not for the overall complex reaction.

Quick Tip to Solve: For a multistep reaction, ask for the rate law to find order; count particles only within one elementary step to find molecularity.

12(d). A first order reaction has a rate constant $2 \times 10^{-3}\,\mathrm{s}^{-1}$. How long will $6\,\mathrm{g}$ of this reactant take to reduce to $2\,\mathrm{g}$? [2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \dfrac{2.303}{k} \log_{10} \dfrac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$, where k is the rate constant and the concentrations refer to the initial state and time t.
- For a fixed volume and the same reactant, concentration is proportional to mass. Therefore the concentration ratio can be replaced by the ratio of initial mass to remaining mass.

Step 1: Identify the initial and remaining amounts The initial mass is $m_0 = 6\,\mathrm{g}$ and the mass remaining is $m_t = 2\,\mathrm{g}$. The rate constant is $k = 2 \times 10^{-3}\,\mathrm{s}^{-1}$. Thus

$$\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = \frac{m_0}{m_t} = \frac{6}{2} = 3.$$

The denominator is the unreacted mass, not the $4\,\mathrm{g}$ already consumed.

Step 2: Substitute in the integrated rate equation Using $\log_{10} 3 = 0.4771$,

$$\begin{aligned} t &= \frac{2.303}{2 \times 10^{-3}} \log_{10} 3 \\ &= \frac{2.303 \times 0.4771}{0.002}\,\mathrm{s} \\ &= 549.38\,\mathrm{s}. \end{aligned}$$

Since k is expressed in reciprocal seconds, the calculated time is in seconds.

Step 3: Conclusion The reactant takes approximately $\boxed{5.49 \times 10^2\,\mathrm{s}}$, or $9.16\,\mathrm{min}$, to decrease from $6\,\mathrm{g}$ to $2\,\mathrm{g}$.

Quick Tip to Solve: For first-order decay, use initial amount divided by amount left inside the logarithm; masses can replace concentrations here.

OR

12(d). The half life for radioactive decay of $^{14}\mathrm{C}$ is 6930 years. An archaeological artifact containing wood had only 75% of the $^{14}\mathrm{C}$ found in a living tree. Find the age of the sample.

[$\log 4 = 0.6021 \quad \log 3 = 0.4771 \quad \log 2 = 0.3010 \quad \log 10 = 1$**]** [2 marks]

Solution:

Concept:

- Radioactive decay follows first-order kinetics: $k = \dfrac{0.693}{t_{1/2}}$, where $t_{1/2}$ is the half-life and k is the decay constant.
- The elapsed time is $t = \dfrac{2.303}{k} \log_{10} \dfrac{N_0}{N_t}$, with N_0 and N_t the initial and remaining numbers of radioactive nuclei in comparable amounts of material.

Quick Tip to Solve: Convert 75% remaining into the ratio $100/75 = 4/3$; then use $\log(4/3) = \log 4 - \log 3$.

Step 1: Calculate the decay constant The half-life of $^{14}\mathrm{C}$ is 6930 years. Hence

$$k = \frac{0.693}{6930} = 1.00 \times 10^{-4}\,\text{year}^{-1}.$$

A living tree provides the initial reference level of $^{14}\mathrm{C}$; after the wood stops exchanging carbon with its environment, its radioactive content decreases by decay.

Step 2: Use the fraction remaining to calculate the age The sample contains 75% of the reference radioactive content, so $N_t = 0.75N_0$ and $N_0/N_t = 4/3$. Using the supplied logarithms,

$$\log_{10}\frac{4}{3} = 0.6021 - 0.4771 = 0.1250,$$
$$t = \frac{2.303}{1.00 \times 10^{-4}}(0.1250)$$
$$= 2878.75\,\text{years}.$$

The age is less than one half-life, as expected because more than half of the original radioactive content remains.

Step 3: Conclusion The archaeological sample is approximately $\boxed{2.88 \times 10^{3}\,\text{years}}$ old.

Quick Tip to Solve: Convert 75% remaining into the ratio $100/75 = 4/3$; then use $\log(4/3) = \log 4 - \log 3$.